

ACTA UNIVERSITATIS CAROLINAE



GEORAMAN 2002

GEOLOGICA

GEOLOGICA
2002, VOL. 46, NO. 1
UNIVERZITA KARLOVA V PRAZE

Acquisitions of reference Raman spectra of minerals concerning research in art or archaeology (prehistoric pigments; alteration products of metals & stained glass)

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A major problem for a relatively "young" discipline such as non-destructive Raman Microscopy (RM) applied to Archaeology and Art in general, i.e. not only pigments ("ARCHAEORAMAN": Smith & Edwards, 1998; Smith, 1999) is the lack of adequate databases of "reference spectra", i.e. spectra obtained from known inorganic, organic or amorphous species. The basis of species identification by RM is the comparison of the spectrum of the unknown material with reference spectra ("Raman spectral fingerprinting"). A poorly-informed database will thus handicap any identification. This is the reason why we prepared this database concerning products susceptible to be observed in three new domains of RM archaeometrical research: the study of Prehistoric pigments (e.g. cave paintings), of corrosion products of metals (e.g. tools), and of pigments and alterations of stained glass (e.g. windows).

We had the opportunity to access the prestigious mineral collections of the Gallery of Mineralogy of the MNHN, but if this chance had certain advantages, it also had certain disadvantages. Thus although we were easily able to obtain more than 70 minerals, it was more difficult to obtain really "pure" samples. Indeed, the mineral samples of the Gallery being natural samples, it was frequent to find one species in association with one or more other species in a rock paragenesis. We observed, for example, samples labelled such as: "goethite/limonite/hematite on galena and blend"; "goethite on siderite"; "manganite and polianite", etc. Even if in most cases it was clear to a mineralogist which phase was which, there were nevertheless several problems of identity. This difficulty often arose without notification on the label of the multiplicity of the phases effectively present; it was the case for example during the analysis of a sample of "anglesite" where the results revealed a rather large quantity of *cerussite* coupled with only a small amount of *anglesite*.

Furthermore, the great opacity of certain minerals analysed in this study, as well as sometimes the Raman selection rules, prevented the acquisition of Raman spectra for this database; in consequence, the samples labelled "chalcocite", "eurubexite + chalcopyrite" (in fact *bornite* by XRD analysis), "acanthite", "galena", "chlorargyrite",

"melanothallite", "percyllite", and "chrysocolla" did not allow the obtention of exploitable spectra.

It may also be argued that the Raman spectrum obtained on various studied minerals can merit the label of "reference spectrum" only if the mineral species identity has definitely been confirmed by another analytical technique. For this reason we analysed by XRD all of our samples that might constitute Raman reference spectra. Thus, if the XRD spectrum corresponds to the name previously given to the sample, the Raman spectrum can then be considered as representative of this mineral species and be labelled as a "reference spectrum". Later, this spectrum, introduced into a Raman database, will allow the identification of an acquired spectrum from a previously-unknown species by Raman spectral fingerprinting. If the XRD spectrum does not correspond to the name previously given to the sample, then two possibilities can be considered:

- (1) If the new XRD identification presents some interest, then the sample is reallocated a correct name and the Raman spectrum is recorded under the new name (ex: the previously-labelled sample "brochantite", turned out to be *antlerite* by XRD).
- (2) If the new XRD identification presents no interest, then one tries to obtain another sample to renew the operation.

It should however be noted that the international XRD database may not necessarily be 100 % correct such that one must be aware of the possibility of error there. Indeed RM is an excellent technique for complementary studies with XRD and might be able to resolve any difficulties arising with the XRD database.

It may also be noted that a method avoiding the need for confirmation by XRD was developed by Smith in his database RAMANITA (Smith & Edwards, 1998; Smith, 2002). There a multitude of spectra from different samples, different spectrometers and different analysts, but of the same "supposed" species, are tabulated and a statistical approach gives a degree of certainty about the identity of the species.

Another major problem which arose during the implementation of this program concerns the nomenclature of mineral species. Indeed, if one considers the year of acquisition of certain studied minerals (this varies between

the beginning of the XIXth century up to today) one may consider that their allocation to such or such mineral species as being really doubtful in many cases. This situation unfortunately arose frequently, but it is however not appropriate to automatically impute these errors of terminology to the mineral collectors, amateurs or professional, who helped in the constitution of the current Gallery. The following examples relate the fragility and the historic inconsistency of the physico-chemical and mineralogical characterizations of mineral species:

- (i) Early in the XIXth century a confusion occurred which disturbed the mineralogical nomenclature of the iron oxyhydroxides *goethite* (alpha-FeOOH) and *lepidocrocite* (gamma-FeOOH); an inversion occurred such that *goethite* was named *lepidocrocite* and inversely. Thus ancient labels may say the opposite of new ones.
- (ii) Jambor (1996) first distinguished two of the polymorphs of formula $\text{Cu}_2\text{Cl}(\text{OH})_3$: paratacamite and clinoatacamite. The confusion between these two polymorphs, whereby many paratacamites were misnamed clinoatacamite, concerns a large number of studies made before 1996. (N.B. There are also two further polymorphs: atacamite and botackallite).

Finally, we may note that the correction of the labelling sometimes appeared to be straightforward (e.g. an official IMA change of name of a species such that samples labelled "*chessylite*" should become "*azurite*" but the old name persists on old labels), or more important as in the case of a sample labelled *brochantite* which is in fact *antlerite*; *langite* which is in fact *brochantite* (with little *langite*); or *xanthosiderite* which turned out to be a mixture of *goethite* and *lepidocrocite*.

Hence we believe that most of the analyses with combined Raman Microscopy and XRD allow the obtention of exact identifications of the minerals.

The existing overall vagueness and the difficulty of establishing a good database of precise reference spectra does not concern only the labelling of the minerals. Further significant problems include:

- (1) The variability of results from different authors for the same analysed species could obviously be due to instrumental differences between the various research teams, but it may well be due to incorrect interpretation of spectra and/or to a false allocation of certain Raman bands. One can quote the excellent work of de Faria et al. (1997) where a certain number of works on oxy-hydroxides of iron are listed: these results are quite eclectic.
- (2) The purity, or even the honesty, of certain commercial samples. The case quoted by Andersen (1982) concerning the pigment "Naples yellow" is very representative. Three supposed commercial samples of $\text{Pb}_2(\text{SbO}_4)_2$ were analysed: the first one gave a lead antimony oxy-hydroxide [$\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$]; the second was constituted by the same hydroxide with Sb_2O_3 in addition; the

third one was composed of PbCO_3 and PbCrO_4 . Thus not one of three samples corresponded to the expected formula.

- (3) Last but not least, the yawning gap of terminological usage between (a) prehistorians/historians, archaeologists and artists, (b) chemists, physicists and spectroscopists, and (c) crystallographers, mineralogists and geologists, is also a major problem. For example if (a) says "vermilion", (b) says "mercury sulphide" or " HgS ", and (c) says "*cinnabar*". Likewise with (a) "ochre" or "red ochre" or "iron ochre"; (b) "iron oxide" or "Fe(III) oxide" or "ferric oxide" or "alpha ferric oxide" or $\alpha\text{-Fe}_2\text{O}_3$; (c) "*hematite*". Only the last is IMA-approved, and it is both necessary and sufficient to define both the chemical composition and the physical structure. Furthermore, the inappropriate names may vary according to the period or the specific recipe of every artist or painter, and many pigments do not have a mineral name (for which a natural occurrence is obligatory under IMA rules), e.g. "Prussian blue" is the ferricyanure of iron [$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$]; "cobalt blue" is the aluminate of cobalt. Here the sentence of Pastoureaux (1990) becomes most fitting: "the colour of the painter is not that of the physicist, and that of the physicist is not that of the poet".

The database described here, which of course is still far from being comprehensive, is presented as an improvement of the pre-existing situation; it provides a battery of spectral data which ought to be of use to researchers working on non-destructive RM analysis of pigments, corroded metals or coloured glass.

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